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ARE SOLUBILITY LIMITS OF IMPORTANCE TO LEACHING?

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This project developed from the Oklo natural fission reactor studies. It had been determined in the Oklo studies that many fission products and actinides remained in the reactor site during the periods of their radioactive decay following formation in the reactor zone two billion years ago. An explanation for this retention of fission products and actinides uses the extreme insolubility of uraninite (UO_2) in very reducing water environments. One can estimate from available thermodynamic data that the concentration of uranium in equilibrium with uraninite in pH 7 water that is free of dissolved oxygen is $\sim 7 \times 10^{-6}$ ppm. This low value suggested that the reducing conditions that can occur in deep geologic burial would result in a very slow leaching of spent fuel elements in contact with water since spent fuel elements are largely sintered UO_2 .

During our studies on the leaching of spent fuel elements we found it difficult to readily duplicate the reducing conditions of deep geologic burial. This result we inferred from the relatively high uranium concentrations that were found in the leachants rather than the low value listed above. However, it was observed that under this reducing condition as well as under an oxidizing atmosphere, that some of the rare earth fission products and actinides behaved differently than the uranium; a behavior we attribute to a precipitation of the rare earths and actinides.

Results of our leaching experiments are shown in Figures 1 and 2. The dissolution was carried out at 25°C under the oxidizing and reducing atmospheres for 65 days. The temperature was then raised to 70°C and the dissolution was continued for an additional 125 days. The results in oxidizing atmosphere are shown as dark lines with the letter O, and those in reducing atmosphere as open

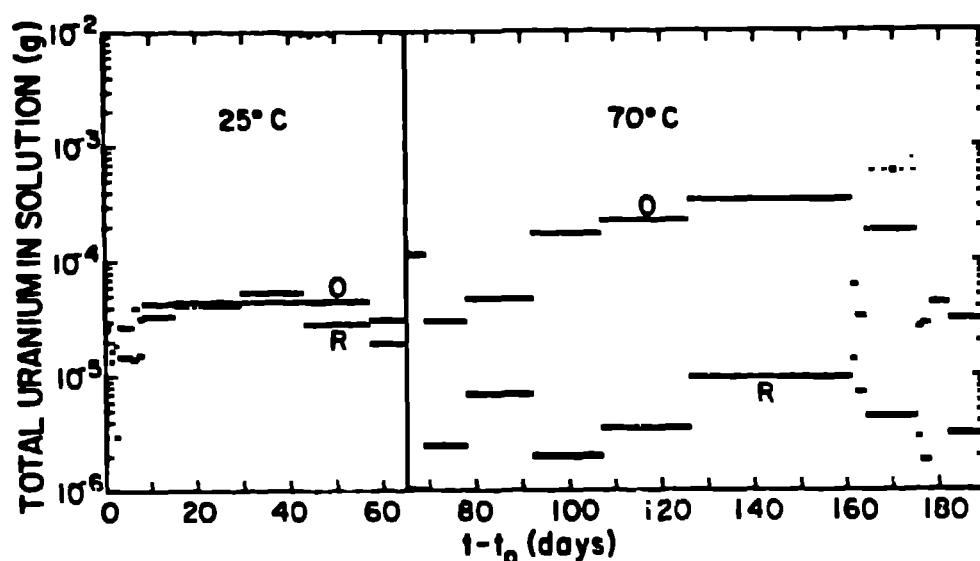


Fig. 1. Uranium concentrations as a function of time.

boxed lines with the letter R. Each line on the graph represents a new volume of leachant that was in contact with the spent fuel element for the period of time shown. The atmospheres were set by bubbling CO₂-free air or 94% argon-6% hydrogen through the leachants. Platinum gauze was also present in the reducing atmosphere experiments. Each element and fission product is treated separately.

Under oxidizing conditions the dissolution of the UO₂ in the spent fuel element appears to be straightforward. At 25°C the concentration of uranium is essentially constant after about 7 day leach periods. Whereas, at 70°C it continues to increase with increasing length of contact time to 35 days. On Fig. 1 are drawn two values (---X---) of the solubility limit of schoepite, UO₃(H₂O), as reported by Holland¹ for 25°C and 90°C. Schoepite is considered^x to be the uranium oxide in equilibrium with water under oxidizing conditions. The uranium concentrations that we measure at 25°C are far from this solubility limit. This is most likely due to slow kinetics of dissolution at 25°C. However, at 70°C the concentrations are much closer to being at the solubility limit. Note that a negative temperature coefficient of solubility was reported by Holland.

At 25°C and reducing conditions the concentration of uranium was also essentially constant for contact periods over 1 week in length. After the temperature was increased to 70°C there was a drop in uranium concentration which increased again as the length of contact time increased. However, after 92 days, there was another drop in concentration with time. It is tempting to attribute this

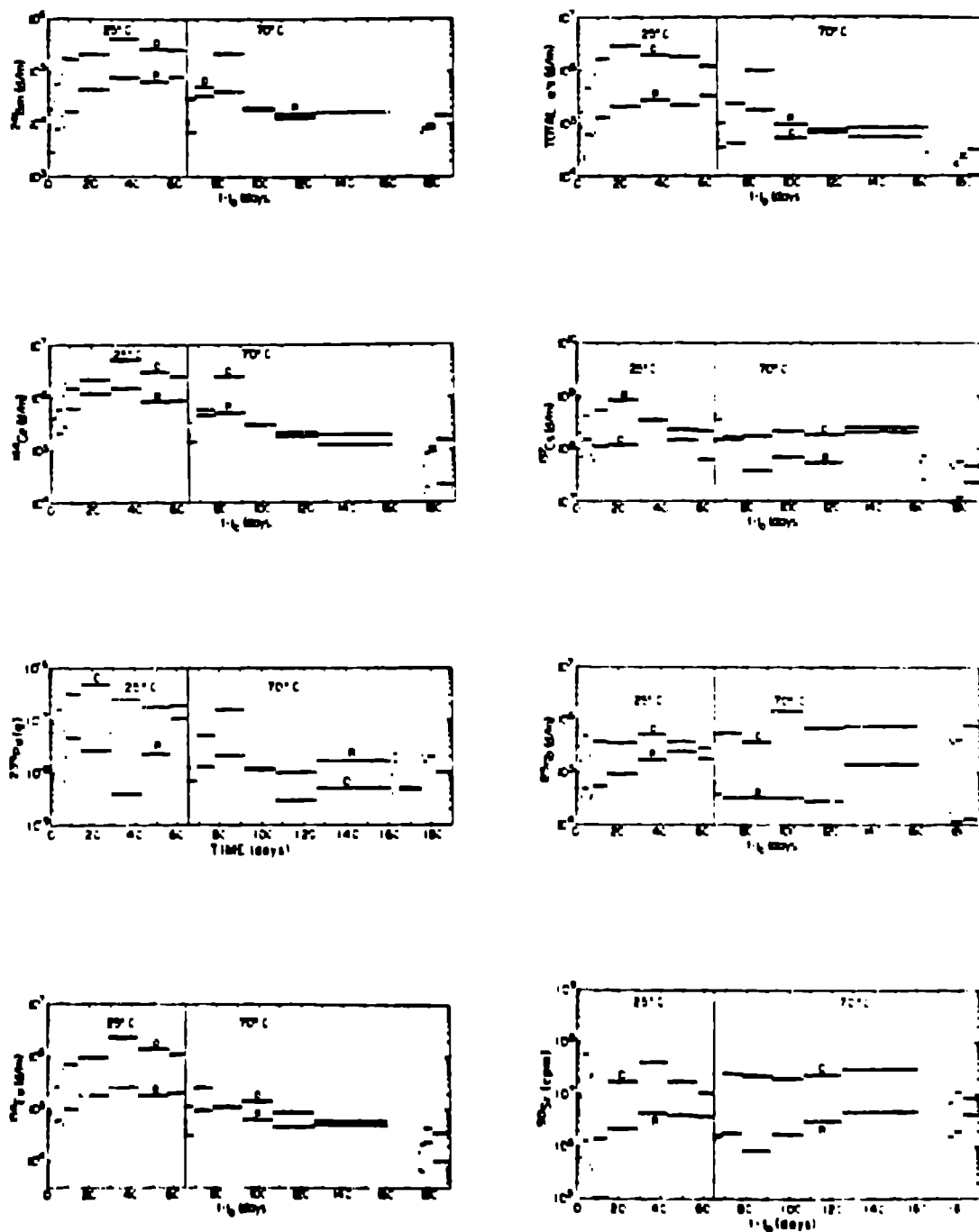


Fig. 2. Fission product and actinide concentrations as a function of time.

erratic behavior to analysis scatter but the same general shape of the graph will be shown in the fission product concentrations (Fig. 2) whose analyses were done on entirely different aliquots.

Figure 2 shows the activities or weight of ^{241}Am , total α 's, ^{154}Eu , ^{144}Ce , and ^{239}Pu that were measured in the leachants. Under oxidizing conditions the concentrations of these radionuclides parallel the results for uranium at 25°C and at 70°C up to and including the sample taken at 92 days. In samples taken after 92 days the concentration of these radionuclides did not increase in the same manner as the concentration of uranium but decreased.

Under reducing conditions the general shape of the plots of concentrations versus time of ^{241}Am , total α 's, ^{154}Eu , ^{144}Ce , and ^{239}Pu are similar to those under oxidizing conditions except that the concentrations under reducing conditions are perhaps a factor of ten lower at 25°C. The difference at 70°C between the two sets of results is even less, but, as in the oxidizing results, the concentrations are lower at 70°C than at 25°C.

If the concentration of uranium and all the radionuclides in the leachant are dependent only on the dissolution of the matrix UO_2 , and all the fission products are homogeneously distributed through the UO_2 , then the ratio of the fission products to uranium in the leachant should be comparable to the calculated radionuclide to uranium ratio in the original spent fuel element. These ratios are listed on Tables 1 and 2 so that the spent fuel element compositions can be compared to the leachant compositions. The 29-43 day sample and the 126-161 day sample were used in calculating the results given in Tables 1 and 2. They were chosen as being the most representative of the 25°C and 70°C experiments. Of these ratios the ones for europium, cerium, americium, and plutonium at 70°C under oxidizing conditions and plutonium at 25°C under reducing conditions are very much lower than the calculated ratios in the spent fuel element. These large differences in the ratios can occur if europium, cerium, americium, and plutonium are at their solubility limits and precipitate as some form of hydrous oxide as the UO_2 matrix continued to dissolve with time.

The data can be used for more quantitative comparisons. The uranium concentrations and activities of the radionuclides were used to calculate isotope concentrations. These isotope concentrations were then converted to elemental concentrations by using the calculated isotopic composition of the H. B. Robinson spent fuel element². The elemental concentrations are listed in Tables 1 and 2 for the same samples whose ratios were listed. Based on the discussion and the data in the Tables, the solubility limits for some of the fission products are listed in Table 3. These numbers assume kinetics did not prevent precipitation at either 25° or 70°C. Also, at 25°C the calculated numbers are largely lower limits since there

TABLE 1
ELEMENT CONCENTRATIONS
REDUCING CONDITIONS

Element	Moles/Liter				Ratio to U				
	25°C		70°C		25°C		70°C		in Fuel
U	4.6	E-5	8.0	E-6					
Eu	7.2	E-9	1.3	E-9	1.6	E-4	1.6	E-4	1.9 E-4
Ce	1.1	E-7	1.4	E-8	2.3	E-3	1.7	E-3	3.6 E-3
Am	1.0	E-8	2.2	E-9	2.2	E-4	2.7	E-4	5.0 E-4
Pu	5.0	E-9	2.8	E-8	1.1	E-4	3.5	E-3	1.3 E-2
Cs	6.6	E-6	4.0	E-6	1.4	E-1	4.9	E-1	4.4 E-3
Sr	1.9	E-7	5.6	E-7	4.2	E-3	7.0	E-2	2.0 E-3
Sb	4.9	E-10	5.2	E-10	1.1	E-5	6.5	E-5	2.1 E-5

TABLE 2
ELEMENT CONCENTRATIONS
OXIDIZING CONDITIONS

Element	Moles/Liter				Ratio to U				
	25°C		70°C		25°C		70°C		in Fuel
U	3.8	E-5	2.8	E-4					
Eu	6.3	E-8	1.6	E-9	1.7	E-3	5.8	E-6	1.9 E-4
Ce	3.8	E-7	8.9	E-9	9.9	E-3	3.2	E-5	3.6 E-3
Am	5.4	E-8	<1	E-9	1.4	E-3	<3	E-6	5.0 E-4
Pu	3.0	E-7	4.8	E-9	7.9	E-3	1.7	E-5	1.3 E-2
Cs	6.6	E-6	3.5	E-6	1.7	E-1	1.0	E-2	4.4 E-3
Sr	1.7	E-6	6.5	E-7	4.5	E-2	2.3	E-3	2.0 E-3
Sb	1.5	E-9	2.2	E-9	4.0	E-5	7.8	E-6	2.1 E-5

Note: Computer notation is used in the Tables. 2.0 E-5 = 2.0×10^{-5} .

TABLE 3
SOLUBILITIES AT pH 4, DEIONIZED WATER

Element	25°C	70°C	Condition
Eu	$\geq 3 \text{ E-8M}$	2 E-9M	O & R
Ce	$\geq 3 \text{ E-7}$	1 E-8	O & R
Am	$\geq 5 \text{ E-8}$	2 E-9	O & R
Pu	3 E-7	1 E-8	O & R
U	$> 5 \text{ E-5}$	$> 3 \text{ E-4}$ $\sim 2 \text{ E-6}$	O R

was not the evidence of precipitation from differences in the spent fuel-leachant ratios. For comparison, we can use the compilations of Baes and Mesmer³ and the calculated solubilities of Newton et al.⁴ Under oxidizing conditions and pH 4 uranium oxide would have a solubility of 10^{-1} to 10^{-2}M and under reducing conditions 10^{-7} to 10^{-11}M depending on which solid, the amorphous or the crystalline, is in equilibrium with the liquid. Similarly the solubility of plutonium oxide would be 10^{-3} to 10^{-7}M for oxidizing and 10^{-7} to 10^{-14}M in reducing conditions. The solubility is not only dependent on the crystal form but also on the actual Eh of the reducing condition. These comparisons are probably as good as one could expect from such a heterogeneous and multicomponent system as a spent fuel element dissolving in water.

The fission products ^{137}Cs , ^{90}Sr , and ^{125}Sb behave differently from the other fission products (Fig. 2). Under reducing conditions and at both 25° and 70°C ^{137}Cs , ^{90}Sr , and ^{125}Sb act similarly to uranium except that, as noted in Table 1, the concentrations of these isotopes in solution are far higher than expected from the isotope to uranium ratio in the spent fuel element. The ratios to uranium at 25° and 70°C for cesium and strontium are very high, especially the cesium to uranium ratios. Katayama et al.⁵ in leaching experiments in air of H. B. Robinson spent fuel elements also found a higher fraction of some radionuclides, especially cesium, in the leachant than in the spent fuel element. They used this higher concentration as indicating an absence of congruent dissolution. Higher concentrations of radionuclides is not by itself sufficient reason to dismiss congruent dissolution. Post-irradiation examinations of spent fuel elements have shown that the radionuclides can be inhomogeneously distributed through the fuel, especially the more volatile elements such as cesium and iodine. If the cesium were concentrated at the grain boundaries

of the fuel and at the colder exterior of the fuel pellet but were still largely incorporated into the UO_2 matrix, its concentration in the leachant would be controlled by the dissolution of the UO_2 matrix but at a higher cesium to uranium ratio. Figs. 1 and 2 indicate the behavior of cesium, strontium, and uranium to be very similar but at different concentration levels.

Conclusions

The solubilities of some radionuclides, especially rare earths and actinides, may be an important and controlling factor in leaching of waste forms. These solubilities should be measured accurately as a function of pH and not as a part of a multicomponent system.

Although the amount of data is small it is interesting to postulate that a negative temperature coefficient of solubility is being exhibited by the actinides and rare earths in Figs. 1 and 2. Individual solubilities should be measured as a function of temperature to determine if a kinetic effect is being observed in the data. A negative temperature coefficient of solubility for actinides and rare earths in water would have important consequences for nuclear reactor safety and for the management of nuclear wastes.

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